

AMSC  
3000  
NCCS-371  
IN-72-CR  
217297  
718

# RECENT ADVANCES IN ELECTRONIC STRUCTURE THEORY AND THEIR INFLUENCE ON THE ACCURACY OF *AB INITIO* POTENTIAL ENERGY SURFACES

Charles W. Bauschlicher, Jr., Stephen R. Langhoff  
NASA Ames Research Center  
Moffett Field, CA 94035  
and  
Peter R. Taylor  
ELORET Institute  
Sunnyvale, CA 94087

N89-26684  
Unclas 0217297  
CSCL 20H G3/72  
(NASA-CR-182895) RECENT ADVANCES IN  
ELECTRONIC STRUCTURE THEORY AND THEIR  
INFLUENCE ON THE ACCURACY OF *AB INITIO*  
POTENTIAL ENERGY SURFACES (NASA. Ames  
Research Center) 21 P

**ABSTRACT.** Recent advances in electronic structure theory and the availability of high speed vector processors have substantially increased the accuracy of *ab initio* potential energy surfaces. The recently developed atomic natural orbital approach for basis set contraction has reduced both the basis set incompleteness and superposition errors in molecular calculations. Furthermore, full CI calculations can often be used to calibrate a CASSCF/MRCI approach that quantitatively accounts for the valence correlation energy. These computational advances also provide a vehicle for systematically improving the calculations and for estimating the residual error in the calculations. Calculations on selected diatomic and triatomic systems will be used to illustrate the accuracy that currently can be achieved for molecular systems. In particular, the  $F+H_2 \rightarrow HF+H$  potential energy hypersurface is used to illustrate the impact of these computational advances on the calculation of potential energy surfaces.

## I. INTRODUCTION

The theoretical determination of purely *ab initio* reaction rates is becoming an important area of computational chemistry research. At NASA Ames Research Center there is considerable interest in determining rates for chemical reactions occurring at high temperatures and in exotic environments. These conditions will be encountered in the re-entry bow shock wave of aero-assisted orbital transfer vehicles (AOTV) [1] or inside the combustion chamber of the hydrogen-fuelled hypersonic craft National Aero-space Plane (NASP) [2]. It is important to have such rate data at the design stage in order to estimate what heating effects will be encountered during re-entry and the combustion efficiency that can be expected under hypersonic conditions. However, it is clearly very difficult (sometimes it is not even possible) to study such environments in the laboratory, and as a result theoretical determinations can provide data that is simply not obtainable by other means.

At present, there is a variety of methodologies [3] for carrying out calculations of reaction cross sections, rate constants and product state distributions. In general, these dynamical methods, either classical or quantum mechanical, are based on knowledge of the potential energy surface (PES), and as a result, the accuracy of the kinetic predictions ultimately depends on the PES itself. Further, those dynamical

methods which rely on a global representation of the PES are conditioned not only by the accuracy of the computed energy points, but also by the techniques used to represent these points with a functional form.

In the present work we shall discuss recent advances in quantum chemical methodology that have improved the reliability of *ab initio* electronic structure calculations. These include full configuration interaction (FCI) calculations [4-13], which have given new insight into the errors associated with the common approximations for treating electron correlation, and atomic natural orbital (ANO) basis sets [14-15], which have reduced the error in the one-particle basis sets by allowing large primitive sets to be contracted with little loss in accuracy. In cases for which it would be unreasonably expensive to apply these techniques over the whole PES, we demonstrate that it should be possible to study the global surface by adjusting a PES based on a lower (and less expensive) level of theory using very accurate calculations performed at the critical points of the surface. It is hoped that surfaces generated in this manner will be sufficiently accurate that comparison with experiment will provide insight into the limitations of the dynamical studies rather than reflect the limitations of the PES itself. This, of course, presupposes that adequate methods for fitting the computed energy points are available [16]; this aspect of the problem is discussed briefly below, but is generally beyond the scope of the present work.

In Section II we give an overview of current theoretical methods. It is not our aim to provide detailed descriptions of methods and algorithms, but rather to discuss the techniques used in broad terms for reference in later discussions. In Sections III and IV we discuss FCI calibration calculations and ANO basis sets, respectively. In Section V, the accuracy of current methods is illustrated by comparing with selected diatomic and triatomic systems where accurate experimental spectroscopic constants are available for comparison. We consider the  $F+H_2 \rightarrow FH+H$  reaction in Section VI, and Section VII contains our conclusions.

## II. QUANTUM CHEMICAL METHODOLOGY

The determination of a PES to be used in computing reaction rates involves solving the non-relativistic time-independent Schrödinger equation for fixed nuclear positions in the Born-Oppenheimer approximation. A review of the general methodology of computational chemistry is given in Ref. 17. The first step in solving the Schrödinger equation is to select a one-particle basis set. This is generally a set of Gaussian-type orbitals (GTOs), grouped into fixed linear combinations called contracted functions. While this type of one-particle basis is universally referred to as an atomic orbital basis, it must be borne in mind that the description it provides of the individual atoms is often far from perfect. This can lead to problems in describing atom-atom interactions or binding, since deficiencies in the "atomic basis" for one atom can be compensated for by using part of the basis on another center, resulting in a completely spurious energy lowering referred to as superposition error (SE) [18]. The effects of superposition error on a computed PES are discussed in more detail below.

Once the one-particle basis has been chosen, a method for solving for the electronic motion must be selected. In principle, the correlation, or  $n$ -particle, problem can be solved exactly in a given one-particle basis set by a full configuration interaction (FCI) calculation, which includes all arrangements of the  $n$  electrons in the given one-particle basis, consistent with Fermi statistics and the desired spin and spatial symmetry. However, the length of the FCI expansion increases factorially

with the number of orbitals and electrons: this generally necessitates the use of methods in which the  $n$ -particle expansion is truncated. The expansion is most commonly truncated by restricting the excitation level to single and double excitations (SDCI) from either a self-consistent field (SCF) or a multiconfigurational SCF (MCSCF) reference wave function. Such an SCF or MCSCF description is the best zeroth-order treatment of the system, and then it is single and double excitations relative to this treatment that formally enter in the next order of perturbation theory. Although much chemistry is well described using an SCF wave function as the reference, an MCSCF zeroth-order wave function is generally required for computing a PES where chemical bonds are formed and broken in order to account for near-degeneracy and multireference effects.

While the SCF description of a system is uniquely defined, the use of an MCSCF wave function introduces an additional degree of freedom, namely, the choice of configurations. Several schemes for choosing configurations have been devised, most of which are based on restricting the multiconfigurational treatment to the bonds or lone-pairs of interest, such as the generalized valence bond (GVB) model and its variants [19]. One simple and widely used scheme is the complete-active-space-SCF (CASSCF) approach [20], in which only a choice of active orbitals and electrons is required: the CASSCF configuration space is then a full CI in this active space. Choosing an active orbital space is usually simpler (and much less error-prone) than constructing a configuration list explicitly. Once the MCSCF configuration space has been defined, it is then necessary to decide on the configuration list for the CI expansion. Several possible routes to such a list exist and it is useful here to distinguish between them.

For the case of a closed-shell single-reference single and double excitation CI (SDCI) calculation, the configuration list is defined unambiguously by considering all configuration state functions (CSFs) in which no more than two electrons occupy virtual orbitals — this is exactly equivalent to including all singly- and doubly-excited CSFs relative to the reference configuration. One approach to multireference SDCI (MRCI) is simply to include all CSFs with no more than two electrons in the virtual orbitals, and if all electrons correlated in the CI calculation are active in the CASSCF calculation this so-called second-order CI (SOCi) corresponds again to all single and double excitations out of the CASSCF configurations as references. However, if there are some electrons correlated in the CI but not active in the CASSCF, these two prescriptions do not lead to the same CI spaces. Specifically, if we take the molecule  $N_2$  as an example, treated with the  $2p$ -derived orbitals and electrons active in the CASSCF, but with all ten valence electrons correlated in the CI, the SOCi wave function would contain some CSFs with, say, two electrons in virtual orbitals and eight electrons in the active orbitals: these are quadruple excitations from the CASSCF configuration space and would *not* be included in a calculation defined as “all single and double excitations from the CASSCF configurations”. While the distinction between these two approaches can be important in terms of computational expense (where SOCi can be considerably more expensive), it is seldom of quantitative significance in practice, and as described above no problem arises when only the CASSCF active electrons are correlated in a subsequent CI.

The construction of the CI configuration list frequently involves problems in addition to those described above. For example, it will often be the case that a CASSCF configuration space of several thousand CSFs, in conjunction with a large one-particle basis, will generate several million or several tens of millions of CSFs in the SOCi (or CASSCF reference MRCI), making such a CI calculation impossible. The most common approach is then to truncate the list of reference configurations,

usually by selecting those configurations with a coefficient in the CASSCF calculation above some threshold. An additional, common, simplification is to eliminate for the CI configuration list any CSFs that have vanishing Hamiltonian matrix elements with all the reference CSFs [21]. This restriction to the so-called "first-order interacting space" can be justified formally by perturbation theory and in practice it seems to result in negligible effects on computed energies and properties. These various approaches to the construction of MRCI configuration lists are discussed in more detail, with numerical examples, below.

Even with truncation of the list of reference CSFs, MRCI calculations can be very costly. Several alternative schemes have therefore been suggested. One approach is to combine together ("contract") CSFs in the MRCI. The "internally contracted" CI method [22], in which the reference CSFs are combined with fixed coefficients to give a single effective reference function has proven to be quite reliable, and with recent improvements [23] is expected to be more commonly used. The "externally contracted" CI (CCI) method of Siegbahn [24], in which the singly- and doubly-excited CSFs are combined using coefficients derived from perturbation theory, has been extensively used and in general is in good agreement with the MRCI results. As we discuss below, a CCI surface, calibrated by very accurate MRCI calculations, may be one of the most cost-effective methods of computing a PES.

Finally, it should be pointed out that the perturbation-theoretic methods [25] (MP2, etc.), used with such success for molecules near their equilibrium geometries, are much less satisfactory when used to compute a PES. Obviously, where several reference configurations are required these single-reference treatments cannot be expected to perform well, and it does not seem possible to overcome such problems by the use of unrestricted Hartree-Fock (UHF) methods to define a single reference CSF: the UHF PES itself will often display discontinuities from spontaneous symmetry breaking, and this inevitably compromises the subsequent perturbation theory treatment. Recent efforts [26] to devise projected UHF-based schemes may overcome these problems, but this is simply another approach to generating a multireference wave function.

Correlation treatments will, of course, approach the FCI result as higher levels of excitations are included. Although explicitly including such higher-excited configurations in the wave function usually leads to a prohibitively long CI expansion, methods of estimating the effects of some of these higher excitations have been developed. For single-configuration-based wave functions these include the Davidson correction [27], the coupled-pair functional (CPF) method [28] (or its modified form, MCPF [29]), and coupled cluster (CC) methods [30]. For the multireference case an extension of the Davidson correction [31] is commonly used. Recent additions to this list of so-called "size-consistent" methods include the quadratic CI (QCI) method [32], which is an approximate (single-reference) CC treatment and the averaged CPF (ACPF) method [33], which is a simple multireference extension of CPF. Finally, the scaled external correlation (SEC) method [34] has been proposed to account for the remaining errors in both the  $n$ - and one-particle expansions.

Estimates of the higher excitations or other approximations can be useful in computing more accurate dissociation energies and barrier heights, especially in systems where more than about eight electrons are correlated. However, these approximate techniques are not bounded variationally like the MRCI, and if the quality of the approximation varies across the PES it may introduce significant "noise" into the computed energies [35]. This should be borne in mind when computed energies are used in fitting a PES, since obtaining a satisfactory fit may

require a high degree of precision in the computed energies. It should be noted in this context that techniques [36] in which selection is performed on *all* the CSFs in the CI expansion, rather than just the reference CSFs (especially those methods in which perturbation theory is used to estimate the contribution of the neglected CSFs) may not always be capable of achieving the necessary precision.

From the above discussion it is clear that what is essentially a double basis set expansion technique for obtaining a wave function may suffer from two interrelated sources of error: the incompleteness of the one- and  $n$ -particle basis sets. FCI calculations, which solve the  $n$ -particle problem exactly for a given one-particle basis set, are therefore extremely useful in that they separate the contributions from these two sources of error. By designing a truncated CI treatment that reproduces the FCI results in a moderate sized basis set (thereby eliminating any error in the  $n$ -particle treatment), accurate results can be obtained by performing the same CI treatment in a very large basis (which minimizes the one-particle basis errors). This general approach has proved very effective in several cases in which accurate experimental data are available for comparison. Atomic natural orbital (ANO) basis sets are particularly useful for studying the saturation of the one-particle basis, as their definition provides a systematic procedure for improving basis set completeness. We next consider in more detail how the FCI method and the ANO basis sets have led to more accurate calculations.

### III. FCI BENCHMARK CALCULATIONS

While this work is directed towards evaluating how recent computational advances have affected the reliability of a computed PES, it is not possible to accomplish this goal by a direct comparison with experimental rate constants. Instead, as the differential correlation effects on a PES are similar to those between different electronic states or between equilibrium and dissociated geometries for a given system, we will use accurate experimental data for diatomic and triatomic systems to evaluate our methods. In addition to comparing with experiment, we also use the FCI results as an absolute standard of comparison for a given one-particle basis set.

Early comparisons of this sort were based on work by Handy and co-workers [37], who developed an efficient direct FCI approach in terms of determinants. Using a double-zeta (DZ) basis set, they considered stretching the O-H bond lengths in the  $\text{H}_2\text{O}$  molecule to 1.5 and 2.0 times their equilibrium values. The FCI results showed that even the restricted Hartree-Fock (RHF) based fourth-order many-body perturbation theory (MBPT) approach [38], which includes the effect of single, double, triple and quadruple excitations, did not accurately describe the stretching of the bond; the error increased from 0.6 kcal/mole at  $r_e$  to 10.3 kcal/mole with the bonds stretched to twice their equilibrium values. Although the MBPT method is rigorously size-consistent and contains the effects of higher than double excitations, it does not describe the bond breaking process well because the RHF reference becomes a poor zeroth-order description of the system as the bond is stretched. Size-consistent methods that include double excitations iteratively — infinite-order methods such as the coupled cluster (CC) approach — do better. However, only methods that account for the multireference character in the wave function as the bonds are broken, such as the CASSCF/MRCI method, provide an accurate description at all bond lengths, or, correspondingly, at all geometries on the PES [39].

The ability to perform FCI calculations was significantly advanced by Sieg-

Table I.  $^1A_1 - ^3B_1$  splitting in  $\text{CH}_2$  (kcal/mole) using a DZP basis set and correlating six electrons.

Method	Splitting	Error
SCF <sup>a</sup>	26.14	14.17
SCF <sup>a</sup> /SDCI	14.63	2.66
SCF/SDCI+Q	12.35	0.38
CPF	12.42	0.45
TCSCF <sup>b</sup> /MRCI	12.20	0.23
TCSCF/MRCI+Q	12.03	0.06
CASSCF <sup>c</sup> /SOCi	11.97	0.00
CASSCF/SOCI+Q	11.79	-0.18
Full CI	11.97	—

<sup>a</sup> The SCF occupations are  $1a_1^2 2a_1^2 3a_1^2 1b_2^2$  and  $1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$ .

<sup>b</sup> SCF treatment for  $^3B_1$  state, two-configuration MCSCF treatment for  $^1A_1$  state (SCF configuration and  $3a_1^2 \rightarrow 1b_1^2$  excitation).

<sup>c</sup> Active space comprises the C 2s 2p and H 1s orbitals.

bahn [40], who formulated the FCI as a series of matrix multiplications to utilize the vector capabilities of current supercomputers, and by Knowles and Handy [41] who effectively eliminated the input/output requirements by formulating the problem in terms of determinants. Using this new FCI approach, a series of benchmark calculations has been performed [4-13], expanding the scope of the earlier studies [37] to include several additional aspects of the effects of electron correlation.

In Table I we compare the FCI  $^1A_1 - ^3B_1$  separation in  $\text{CH}_2$  with various truncated CI results [4]. Since the  $^1A_1$  and  $^3B_1$  states are derived nominally from the  $^3P$  and  $^5S$  states of carbon, respectively, the different bonding mechanisms result in a substantial correlation contribution to the separation: the SCF separation is over 14 kcal/mole too large. The error of 2.7 kcal/mole at the SDCI level is still relatively large; an error of this magnitude in a barrier height, for example, could result in significant errors in a computed reaction rate. The inclusion of the contribution of unlinked higher excitations through either the Davidson correction (+Q) or the CPF method reduces the error substantially. The origin of the error in the SCF/SDCI treatment is the second important configuration, arising from the double excitation  $3a_1^2 \rightarrow 1b_1^2$ , in the  $^1A_1$  state. If the orbitals for the  $^1A_1$  state are optimized in a two-configuration SCF (TCSCF) calculation, and correlation is included by performing an MRCI calculation based on both these reference configurations, the error is about half that of the SDCI+Q or CPF treatments. The error is reduced to only 0.06 kcal/mole if the multireference analog of the +Q correction is added. After the  $3a_1^2 \rightarrow 1b_1^2$  excitation, the next most important correlation effect is that associated with the C-H bonds. If this correlation effect is accounted for in both the CASSCF zeroth-order reference and a subsequent SOCI calculation, essentially perfect agreement between the SOCI and FCI is observed. That is, a well-defined CASSCF/MRCI treatment accounts for all of the differential correlation effects. It is interesting to note that adding the multireference +Q correction to the SOCI energy results in an overcounting of the effect of higher excitations and

Table II.  $N_2$   $^1\Sigma_g^+$  spectroscopic constants

Method	$r_e$ ( $a_0$ )	DZP basis 6 electrons correlated	$D_e$ (eV)
		$\omega_e$ ( $\text{cm}^{-1}$ )	
SDCI	2.102	2436	8.298
SDCI+Q	2.115	2373	8.613
SDTCI	2.107	2411	8.462
SDTQCI	2.121	2343	8.732
SDQCI	2.116	2361	8.586
CPF	2.112	2382	8.526
MCPF	2.114	2370	8.556
SOCI	2.123	2334	8.743
SOCI+Q	2.123	2333	8.766
Full CI	2.123	2333	8.750

the separation becomes smaller than the FCI result.

We next consider the spectroscopic constants [5] for the ground state of  $N_2$ , which are summarized in Table II. The SDCI calculation yields a bond length that is in good agreement with the FCI, but the error in  $D_e$  is 0.45 eV, even when size-consistency problems are minimized by using the  $^7\Sigma_u^+$  state of  $N_2$  to represent two ground state  $N(^4S)$  atoms at infinite separation. Although the addition of quadruple excitations, either variationally (SDQCI) or by the +Q, CPF or MCPF approximations, further reduces the error in  $D_e$ , it remains too large for chemical accuracy (1 kcal/mole). If both triple and quadruple excitations are included, the spectroscopic constants are all in good agreement with the FCI. However, this level of treatment is prohibitively expensive in a large one-particle basis set, and even this wave function does not dissociate correctly to ground state atoms, as this requires six-fold excitations relative the SCF configuration at  $r_e$ . The spectroscopic constants computed from an SOCI treatment based on a CASSCF wave function are in excellent agreement with the FCI. Furthermore, this treatment agrees with the FCI for all  $r$  values. The addition of the +Q correction does not affect  $r_e$  or  $\omega_e$ , but it makes  $D_e$  too large compared with the FCI.

Dipole-induced dipole or dipole-quadrupole interactions can give rise to weakly bound complexes of considerable importance in dynamical studies. It is therefore important that properties such as the polarizability can be accurately determined. A FCI study [6] of the polarizability of  $F^-$  is summarized in Table III. As in the previous examples, the SDCI treatment is not sufficiently accurate for very high quality calculations. The inclusion of an estimate of higher excitations improves the results; in this case CPF is superior to the +Q correction. In the multireference case two different approaches were used. In the first, the CASSCF included the  $2p$  electrons and  $2p$  and  $3p$  orbitals in the active space, and all CASSCF CSFs were used as references for the CI, in which the  $2s$  and  $2p$  electrons were correlated. Results obtained in this way are denoted MRCI in Table III. A more elaborate CASSCF calculation, with the  $2s$  and  $2p$  electrons and the  $2s$ ,  $3s$ ,  $2p$  and  $3p$  orbitals in the active space, was also performed: the use of all these CASSCF CSFs as references gives an SOCI expansion and the results are denoted SOCI in

Table III. Polarizability of  $F^-$  (a.u.)

Method	DZP + diffuse <i>spd</i> basis
	8 electrons correlated, $\alpha = d^2 E/dF^2$
	$\alpha$
SDCI	13.965
SDCI+Q	15.540
CPF	16.050
MRCI	16.134
MRCI+Q	16.346
SOCI	16.034
SOCI+Q	16.303
Full CI	16.295

Table III. The MRCI and SOCI results are not in as good agreement with the FCI as the MRCI+Q or SOCI+Q results. The +Q correction does not overshoot as it did for  $N_2$  and  $CH_2$ , in part because of the larger number of electrons correlated here. As noted above, when only six electrons are correlated, the MRCI accounts for such a high percentage of the correlation that the +Q correction overestimates the missing correlation. For more than six electrons, or for cases where the zeroth-order wave function used is less satisfactory than was the CASSCF for  $N_2$  and  $CH_2$ , the +Q correction may become a better approximation. This is especially true where quantities involving large differential correlation effects, such as electron affinities, are sought [7]. Thus the +Q correction substantially improves the agreement with FCI for the electron affinity of fluorine [8], even if large CASSCF active spaces and SOCI wave functions are employed.

It is almost always the case that only the valence electrons are correlated in quantum chemical studies, although for very accurate results core-valence and core-core correlation effects may be required. A recent detailed study [9] has shown that it is very difficult to find a truncated CI treatment that satisfactorily reproduces FCI correlation energies including core correlation. If the main interest is in a differential effect of core correlation (such as the contribution to an energy separation or to a bond length) it may be possible to neglect the core-core correlation, which is often almost independent of geometry, and to compute only the core-valence correlation. This is most easily accomplished by eliminating from the CI expansion any CSFs corresponding to a double (or higher) excitation from the core orbitals. Such an approach seems to recover most of the core correlation contribution to spectroscopic constants. While the effects of core correlation are often small (a few tenths kcal/mole in the  $CH_2$  singlet/triplet separation, for example [9]), they may be important if accuracy better than about one kcal/mole is desired. In view of the expense incurred by including the core electrons in the CI treatment, and the additional problem that correlating more electrons increases the need for size consistency, it may be preferable to handle core-valence correlation effects by an effective potential approach like that developed by Meyer and co-workers [42].

Most scattering formalisms are developed in a diabatic representation, whereas a theoretical PES is computed in the adiabatic representation. Hence when curve crossings (or more complicated phenomena for polyatomic systems) occur both potentials must be accurately represented in the crossing region, and nonadiabatic cou-



pling matrix elements (NACMEs) will be required to define the unitary transformation between the diabatic and adiabatic representations. Until recently, NACMEs were computed either using finite difference methods [43] or via approximations to avoid computing matrix elements between non-orthogonal wave functions [44]. However, Lengsfeld, Saxe, and Yarkony [45] have recently developed an efficient method of evaluating NACMEs based on state-averaged MCSCF wave functions and analytic derivative methods. This should provide NACMEs of the same overall accuracy as that obtained for the adiabatic potentials.

In curve crossings where the molecular orbitals for the two states are similar, such as interactions between valence states derived from different asymptotic limits, the CASSCF/MRCI approach would be expected to describe both potentials accurately irrespective of which state is used for the orbital optimization. However, when the character of the two states is very different, such as valence/Rydberg mixing [10] or interaction between states derived from ionic and covalent limits [11], it is more difficult to achieve equivalent accuracy for the lowest adiabatic state on either side of the crossing point. This is commonly the case for charge-exchange reactions, such as  $N^+ + N_2 \rightarrow N + N_2^+$ , or chemi-ionization processes such as  $M + X \rightarrow M^+ + X^-$ , where the optimal molecular orbitals for the ionic and neutral solutions differ greatly. To gain additional insight into the computational requirements for describing the potentials in the region of curve crossings, we have studied [11] the  $Li + F \rightarrow Li^+ + F^-$  chemi-ionization process using the FCI approach. In LiF the lowest adiabatic state at short  $r$  values, namely the ionic  $X^1\Sigma^+$  state, dissociates adiabatically to neutral ground state atoms. There is an avoided crossing at the point where the energy difference between the F electron affinity (EA) and the Li ionization potential exactly balances the  $1/r$  electrostatic stabilization. Since the CASSCF description of  $F^-$  is poor [8], the CASSCF estimate for the bond distance at the crossing point is unrealistically small. When orbitals from the ground-state CASSCF wave function are used to construct an MRCI wave function, this problem with the CASSCF description of the crossing point will compromise the accuracy of the MRCI description. This problem is not easily resolved by expanding the CASSCF active space, as very large active spaces are required to obtain a good description of atomic electron affinities. However, by performing instead a state-averaged CASSCF calculation, in which the orbitals are optimized for the average of the two lowest  $^1\Sigma^+$  states in LiF (the ionic and neutral states), the orbital bias is eliminated and the MRCI treatment is in excellent agreement with the FCI. It is also important to note that this averaging does not significantly degrade the description of the system near  $r_e$ . Thus state averaging appears to be an excellent method of achieving equal accuracy for two potential curves in a curve crossing region, and should also perform well for polyatomic systems. The utility of state averaging as a means of obtaining a good compromise orthogonal set of molecular orbitals for use in an MRCI wave function has also been found to be an excellent route to computing accurate electronic transition moments [12]. It is thus seen that there is much in common between methods that account accurately for differential correlation effects on a PES and those that yield accurate spectroscopic constants and molecular properties.

A number of important conclusions can be drawn from these FCI benchmark studies. First, even in a complete one-particle basis set, it is unlikely that an accurate PES can be generated using single-reference-based treatments such as SCF/SDCI. If all regions of a PES are well described by an SCF reference, SDCI+Q, CPF or CC methods should yield acceptable results, but this is a very uncommon

situation in practice. Second, the CASSCF/MRCI method is capable not only of achieving high accuracy for an individual PES, but also of achieving equivalent accuracy for several PES derived from different asymptotic limits. Some questions remain as to the utility of including the multireference +Q correction: it probably should not be included when six or fewer electrons are correlated and the CASSCF active space contains all the important correlation effects, since a large percentage of the higher excitations are already accounted for in the MRCI and any correction then overshoots the FCI. For more than six electrons correlated, the true answer may be closer to the +Q corrected value, although even here for systems that are very well described at the CASSCF level the +Q correction to MRCI may result in some overshoot. For relatively large numbers of electrons correlated (say, more than 12) or cases where there are large differential correlation effects, such as those encountered in the computation of electron affinities, the +Q may *underestimate* the importance of higher excitations. Thus, it is generally most important to include the +Q correction when there is a significant change in the character of the system that is not well described at the CASSCF level. Such a situation arises, for example, for the reaction  $F+H_2 \rightarrow HF+H$ , where F in the HF product has some  $F^-$  character. This is discussed further below when this reaction is considered in detail.

#### IV. ANO BASIS SETS

In the previous section we showed that the CASSCF/MRCI approach yields results in excellent agreement with FCI, that is, near the  $n$ -particle limit. We may therefore expect excellent agreement with experiment when the CASSCF/MRCI approach is used in conjunction with extended one-particle basis sets. It has become clear [46] that, until recently, the basis set requirements for achieving the one-particle limit at the correlated level were commonly underestimated, both in the number of functions required to saturate the space for each angular momentum quantum number and in the maximum angular momentum required. For the segmented basis sets that are widely used in quantum chemistry, improving the basis set normally involves replacing a smaller primitive basis set with a larger one. It is then seldom possible to guarantee that the smaller basis spans a subspace of the larger set, and it is thus difficult to establish how results obtained with different basis sets relate to convergence of the one-particle space. Ideally, the possibility of differences in primitive basis sets would be eliminated by using a single (nearly complete) primitive set, contracted in different ways such that the smaller contracted sets are subsets of the larger one. Such an approach requires a general contraction scheme, such as the one proposed by Raffanetti [47] for contracting valence orbitals at the SCF level. However, a contraction based on atomic SCF orbitals is not necessarily suitable for handling the correlation problem, and provides no means to contract polarization functions, large primitive sets of which are required for accurate results. Calculations on molecular systems have shown [48] that natural orbitals (NO) provide an efficient method of truncating the orbital space in correlated treatments. Almlöf and Taylor [14] have proposed a NO procedure for contracting atomic basis sets suitable for use in correlated molecular calculations: this atomic natural orbitals (ANO) approach is an efficient method for contracting large primitive valence and polarization basis sets. It has the advantage that the natural orbital occupation numbers provide a criterion for systematically expanding the basis set.

These ideas are illustrated for N atom and  $N_2$  in Table IV. As the contraction of the (13s 8p 6d) primitive set is expanded from [4s 3p 2d] to [5s 4p 3d] to [6s 5p 4d],

Table IV. N/N<sub>2</sub> extended basis total energies ( $E_H$ ) and “dissociation energies” (eV).

N atom				
Basis set	$E_{SCF} + 54.$	$\epsilon_{corr}$		
(13s 8p 6d)	-0.400790	-0.111493		
[6s 5p 4d]	-0.400779	-0.111321		
[5s 4p 3d]	-0.400769	-0.110925		
[4s 3p 2d]	-0.400725	-0.109066		
(13s 8p 6d 4f)	-0.400790	-0.121385		
[5s 4p 3d 2f]	-0.400769	-0.120499		
[4s 3p 2d 1f]	-0.400725	-0.117584		
[5s 4p 3d 2f] (2g) <sup>a</sup>	-0.400769	-0.122472		
[5s 4p 3d 2f 1g]	-0.400769	-0.122138		
N <sub>2</sub> molecule <sup>b</sup>				
Basis set	$E_{SCF} + 108.$	$\epsilon_{corr}$	$D_e(SCF)$	$D_e(SDCI)$
(13s 8p 6d)	-0.986307	-0.338118	5.03	8.16
[6s 5p 4d]	-0.985913	-0.337304	5.02	8.14
[5s 4p 3d]	-0.984833	-0.335395	4.99	8.08
[4s 3p 2d]	-0.983483	-0.329330	4.95	7.98
(13s 8p 6d 4f)	-0.989318	-0.365735	5.11	8.45
[5s 4p 3d 2f]	-0.988031	-0.362548	5.07	8.38
[4s 3p 2d 1f]	-0.986230	-0.353283	5.03	8.24
[5s 4p 3d 2f] (2g) <sup>a</sup>	-0.988458	-0.370808	5.09	8.51
[5s 4p 3d 2f 1g]	-0.988322	-0.369270	5.08	8.48

---

<sup>a</sup> 2 uncontracted *g* sets.

<sup>b</sup>  $r(N-N) = 2.1 a_0$ , 10 electrons correlated.

the correlation energy systematically converges to that of the uncontracted results. The same is true for the (4f) and (2g) polarization sets. When these ANO sets are applied to N<sub>2</sub>, the same systematic convergence of  $D_e$  is observed. In addition, by contracting the basis set for the atom, the superposition errors at the correlated level are minimized.

In order to treat atomic states with different character equally, e.g. F and F<sup>-</sup>, the ANOs can be averaged to yield a compromise set. This is analogous to the state averaging used to define compromise orbitals suitable for describing molecular states of different character discussed above. A [5s 4p 3d 2f 1g] contraction based on the average of F and F<sup>-</sup> has an SDCI level EA that agrees with the uncontracted (13s 9p 6d 4f 2g) basis set result to within 0.01 eV [49]. This can be compared with a 0.1 eV error for the same size basis set that is contracted for F alone, but with the outermost (the most diffuse) *s* and *p* primitive functions uncontracted.

Table V.  $^1A_1 - ^3B_1$  splitting in  $\text{CH}_2$  (kcal/mole)

SOC1: six electrons correlated	
Basis	Separation
$[3s\ 2p\ 1d/2s\ 1p]$	11.33
$[4s\ 3p\ 2d\ 1f/3s\ 2p\ 1d]$	9.66
$[5s\ 4p\ 3d\ 2f\ 1g/4s\ 3p\ 2d]$	9.13
Expt ( $T_0$ )	9.02 ( $\pm 0.01$ )
Expt+Theory <sup>a</sup> ( $T_e$ )	9.28 ( $\pm 0.1$ )

<sup>a</sup> Ref. 53.

The results are better if the contraction is based on  $F^-$  alone, but they are still not as good as those obtained by using the average ANOs. ANO basis sets averaged for different states should thus supply a more uniform description in cases in which there is charge transfer or ionic/covalent mixing. It should be noted, however, that it may still be necessary to uncontract the most diffuse primitive functions and/or add extra diffuse functions to describe properties such as the dipole moments and polarizabilities [15,50] that are sensitive to the outer regions of the charge density.

## V. CALIBRATION CALCULATIONS

The FCI benchmark calculations discussed in Section III show that a CASSCF/MRCI treatment is capable of accurately reproducing the FCI results, at least when six electrons or fewer are correlated. Further, the ANO basis sets discussed in Section IV show that it is now possible to contract nearly complete primitive sets to manageable size with only a small loss in accuracy. Therefore, a six electron CASSCF/MRCI treatment performed in a large ANO basis set is expected to reproduce accurately the FCI result in a complete one-particle basis set, and hence should accurately reproduce experiment. By including the +Q correction, we believe chemical accuracy should be achievable for eight electron systems. In this section we illustrate several calculations that have achieved unprecedented accuracy by combining FCI benchmarks and ANO basis sets.

As discussed above, FCI calculations for  $\text{CH}_2$  show that the SOC1 treatment accurately accounts for the differential correlation contribution to the  $\text{CH}_2$   $^1A_1 - ^3B_1$  separation. In Table V, this level of treatment is performed using increasingly accurate ANO basis sets [51]. It is interesting to note that although the  $[4s\ 3p\ 2d\ 1f/3s\ 2p\ 1d]$  basis contains fewer contracted functions than the large segmented basis sets previously applied to this problem [52], it produces a superior result for the separation. The largest ANO basis set used gives a separation in good agreement with, but smaller than, the  $T_e$  value deduced from a combination of theory and experiment [53]. From the convergence of the result with expansion of the ANO basis set, it is estimated that the valence limit is about  $9.05 \pm 0.1$  kcal/mole. The remaining discrepancy with experiment is probably due to core-valence correlation effects. While FCI calculations have shown that a high level of correlation

Table VI.  $N_2$   $^1\Sigma_g^+$  spectroscopic constants

Method	[5s 4p 3d 2f 1g] basis		
	$r_e$ (Å)	$\omega_e$ (cm $^{-1}$ )	$D_e$ (eV)
SOCI(6)	1.096	2382	10.015
SOCI(6)+Q	1.096	2382	10.042
MRCI(10)	1.101	2343	9.723
MRCI(10)+Q	1.102	2336	9.745
Expt <sup>a</sup>	1.098	2359	9.905

<sup>a</sup> Ref. 58.

treatment is required for an accurate estimate of the CV contribution to the separation, somewhat simpler theoretical calculations [9] place an upper bound on this quantity of a 0.35 kcal/mole increase in the separation. Therefore, it is clearly possible to achieve an accuracy of better than one kcal/mole in the singlet-triplet separation in methylene.

An analogous study [51] for  $SiH_2$  indicates that the singlet-triplet splitting can also be accurately computed for this second-row molecule. However, it now becomes necessary to include the dominant relativistic contributions, namely the mass-velocity and Darwin terms [54], via first-order perturbation theory [55] or by using an effective core potential, if chemical accuracy is to be achieved. Once relativistic effects have been accounted for, an accuracy of about 0.2 kcal/mole is obtained. This incidentally establishes the ionization potential of the  $^1A_1$  state of  $SiH_2$  as 9.15 eV, the higher of two recent experimental values [56]. The ability to treat second-row systems accurately can have some advantages when comparing with experiment: for example, molecules containing Cl can be isotopically substituted, while the corresponding F species cannot. This will often mean that more information is available for comparison for some second-row systems.

The FCI study of the  $X^1\Sigma_g^+$  state of  $N_2$  showed that the SOCI treatment correlating the six 2p electrons, SOCI(6), accounts for essentially all of the correlation effects on the spectroscopic constants. However, this treatment [57] in a large ANO basis set produces a  $D_e$  value that is larger than experiment [58] (see Table VI). Since this basis set has virtually no CI superposition error, this conclusively shows that 2s correlation reduces the  $D_e$  value. The inclusion of 2s correlation, i.e. correlating ten electrons, results in a  $D_e$  that is 0.16 eV smaller than experiment. The decrease in  $D_e$  when the 2s electrons are correlated can be explained in terms of an important atomic correlation effect that has no analog in the molecular system, namely the  $2s \rightarrow 3d$  excitation with a recoupling of the 2p electrons. At the MRCI(10) level (this is based on the CASSCF reference space from the six-electron calculation) the error in  $D_e$  is about 4 kcal/mole, or larger than the 1 kcal/mole desired for chemical accuracy. We may thus expect that computations on reactions involving multiply-bonded systems will have relative errors of several kcal/mole, in spite of the recent improvements in methodology. On the other hand, it is still important to apply the most accurate techniques to such problems, since certain

Table VII. FCI calibration of the classical barrier height of  $F+H_2 \rightarrow HF+H^a$ .

A. At the FCI saddle point		
	barrier	exothermicity
FCI	4.50	28.84
MRCI(300)	5.18	28.57
MRCI(300)+Q	4.43	29.12
MRCI(322)(0.05)	5.00	29.12
MRCI(322)(0.05)+Q	4.32	29.21
MRCI(322)(0.025)	4.73	29.17
MRCI(322)(0.025)+Q	4.51	28.80
MRCI(322)(0.01)	4.71	29.19
MRCI(322)(0.01)+Q	4.54	28.84
MRCI(522)(0.025)	4.55	29.41
MRCI(522)(0.025)+Q	4.32	29.31

  

B. At the optimized saddle-point geometry <sup>b</sup>				
	r(F-H)	r(H-H)	barrier	exothermicity
FCI	2.761	1.467	4.50	28.84
CPF	2.801	1.467	4.40	26.47
MRCI(300)	2.740	1.476	5.16	28.57
MRCI(300)+Q	2.795	1.467	4.42	29.12
MRCI(322)(0.025)	2.761	1.474	4.70	29.17
MRCI(322)(0.025)+Q	2.755	1.475	4.49	28.80

<sup>a</sup> Energies in kcal/mole and bond lengths in  $a_0$ . All calculations are done using the [4s3p1d/2s1p] basis set and correlating seven electrons. The barrier is referenced to  $F \dots H_2(50a_0)$ , and the exothermicity is computed using  $HF \dots H(50a_0)$ .

<sup>b</sup> Geometry optimizations were done using a biquadratic fit to a grid of nine points.

aspects, such as understanding the effect of 2s correlation in reducing the  $D_e$  of the  $X^1\Sigma_g^+$  state of  $N_2$ , are a by-product of accurate, calibrated calculations. We hope that similar insights will occur in the study of dynamics that are based on a PES using these recent advances in electronic structure theory.

## VI. THE $F+H_2 \rightarrow HF+H$ REACTION

In the previous section we showed that CASSCF/MRCI treatments of electron correlation in large ANO basis sets give spectroscopic constants that are in excellent agreement with experiment. We now discuss the application of these methods to computing the barrier height and exothermicity of the  $F+H_2 \rightarrow HF+H$  reaction.

In Table VII, several different MRCI treatments are compared to the FCI barrier height and exothermicity [13,59]; in all of these treatments only the seven F 2p and H 1s valence electrons are correlated. The smallest MRCI treatment has the F 2p $\sigma$  and H 1s orbitals active in the CASSCF and MRCI (denoted MRCI(300),

since there are three active orbitals of  $a_1$  symmetry). This calculation yields a barrier height that is 0.68 kcal/mole higher than the FCI. The inclusion of the +Q correction improves the barrier height, but it is now slightly too small. The sign of the error in the exothermicity also changes with the addition of the +Q correction. Such problems with the MRCI(300) treatment are not unexpected since the HF wave function is known to contain significant  $H^+F^-$  character. For accurate results it is therefore necessary to improve the description of the electron affinity (EA) of F by expanding the active space to (322) to include  $2p \rightarrow 2p'$  correlation. With such an active space a very large number of CSFs would arise in a CASSCF reference MRCI (or an SOCI) wave function, so it becomes necessary to select reference CSFs according to their CASSCF coefficients as described in Section II: this expanded active space yields MRCI(322)+Q results that are in excellent agreement with the FCI, provided that the threshold for including CASSCF CSFs as references is no larger than 0.025. As noted above, further expansion of the active space improves the results, but the +Q correction may now overshoot the FCI value.

The MRCI(300)+Q and MRCI(322)(0.025)+Q saddle-point geometries are both in excellent agreement with the FCI value. It is interesting to note that although the CPF method is quite accurate for the barrier height and saddle-point geometry, it is significantly poorer for the exothermicity.

In order to compute an accurate barrier height, the basis set is expanded from the  $[4s\ 3p\ 1d/2s\ 1p]$  set used for the FCI calibration to a  $[5s\ 5p\ 3d\ 2f\ 1g/4s\ 3p\ 2d]$  ANO set. In this large basis set, the spectroscopic constants for  $H_2$  are in almost perfect agreement with experiment. The MRCI(222)+Q treatment of HF, which is analogous to the MRCI(322) treatment of  $F+H_2$ , yields an excellent  $r_e$ , but a  $D_e$  which is 1.22 kcal/mole (0.05 eV) too small. The CI superposition error for F in the  $H_2$  ghost basis set is 0.15 kcal/mole; this is even smaller than that obtained using the large Slater-type basis set from Ref. 60. An accuracy of better than 1 kcal/mole for the barrier height can therefore be expected.

The theoretical results for the classical saddle-point and barrier height are summarized in Table VIII. Based on the FCI calibration, the MRCI(322)(2p)+Q calculations, in which seven electrons (i.e. excluding F 2s) are correlated, are expected to reproduce the result of an FCI calculation in a nearly complete one-particle basis set. Since F 2s correlation decreases the barrier, this MRCI(322)(2p)+Q barrier, when corrected for the CI superposition error (SE), represents an absolute upper bound of 2.52 kcal/mole for the barrier.

The inclusion of F 2s correlation decreases the barrier height, and increases the magnitude of the +Q correction. Unfortunately, it is not possible to calibrate this level of treatment using the FCI approach. However, the nine electron +Q correction must be at least as large as the seven electron +Q correction, which is calibrated against the FCI. Therefore, a conservative upper bound of 2.26 kcal/mole is obtained using the MRCI(322)(2p)+Q treatment (corrected for SE). However, experience for nine electron systems, especially in calculations of electron affinities, has shown that the +Q correction for nine electrons is probably somewhat too small, making the actual MRCI(322)+Q value of 1.86 kcal/mole (corrected for SE) a more realistic estimate. Finally, the best estimate should also include an estimate of basis set incompleteness and account for the underestimation of the effects of higher excitations by the +Q correction. To accomplish this, we first omit the SE correction, assuming instead that the basis set incompleteness is 0.1 kcal/mole, and we further assume that the true +Q correction is 120% of that computed; this yields our best empirical estimate of 1.35 kcal/mole for the classical barrier height. Thus

Table VIII. Theoretical studies of the classical saddle-point geometry and barrier for the F+H<sub>2</sub> reaction.

Basis <sup>a</sup>	Level of treatment	saddle-point		barrier <sup>b</sup>	exothermicity <sup>b</sup>
A	MRCI(322)(2p) <sup>c</sup>	2.899	1.455	2.99	33.96
A	MRCI(322)(2p)+Q <sup>c</sup>	2.910	1.456	2.42	33.42
A	MRCI(322)	2.914	1.451	2.63	31.61
A	MRCI(322)+Q	2.950	1.450	1.66	30.47
A	CCI(322)	... <sup>d</sup>	... <sup>d</sup>	2.79	31.8
A	CCI(322)+Q	... <sup>d</sup>	... <sup>d</sup>	2.02	30.7
A+H(f) <sup>e</sup>	CCI(322)	... <sup>d</sup>	... <sup>d</sup>	2.73	
A+H(f)	CCI(322) +Q	... <sup>d</sup>	... <sup>d</sup>	1.95	
A-F(g)	CCI(322)	2.879	1.447	2.89	
A-F(g)	CCI(322)+Q	2.909	1.445	2.14	
	Expt.				31.73

<sup>a</sup> This letter "A" denotes the [5s5p3d2f1g/4s3p2d] basis described in the text.

<sup>b</sup> The barrier is referenced to F...H<sub>2</sub>(50a<sub>0</sub>), and the exothermicity is computed using HF...H(50a<sub>0</sub>).

<sup>c</sup> These are seven-electron treatments (i.e. 2s correlation is excluded).

<sup>d</sup> The MRCI(300)+Q saddle point geometry is used, r(F-H)=2.921 a<sub>0</sub> and r(H-H)=1.450 a<sub>0</sub>.

<sup>e</sup> Denotes that a function of this angular momentum type has been added.

based solely on estimates from *ab initio* calculation the barrier height should be between 1.35 and 1.86 kcal/mole.

While the MRCI(322)+Q calculations in the ANO basis set are more reliable than any previous results, considerable computer time would be required to compute a global surface at this level. The barrier height was therefore investigated using the contracted CI (CCI) approach. In the same ANO basis set, the CCI+Q barrier is 0.4 kcal/mole higher than the corresponding MRCI+Q value. Further extension of the basis set was also investigated at the CCI level: *f* polarization functions on H were found to lower the barrier by only 0.07 kcal/mole, while eliminating the *g* function on F increased the barrier by 0.12 kcal/mole. These observations are consistent with the contention that the basis set is nearly complete. The CCI calculation in this basis set is sufficiently inexpensive that much larger regions of the PES can be investigated. Of course, given the differences between the MRCI and CCI barrier heights some account would have to be taken of the errors in CCI treatment; this might involve adjusting the parameters in the fitted potential based on the MRCI(322)+Q calculation or on information deduced from experiment.

While the MRCI(322)+Q-corrected CCI+Q PES should be accurate, direct comparison with experiment is difficult. To facilitate comparison we have employed canonical variational transition state theory [61] at the classical and adiabatic barrier using the CCI+Q potential for both F+H<sub>2</sub> and F+D<sub>2</sub>. These calculations account for the zero-point energy and include a tunneling correction. The results of these calculations are summarized in Table IX. As expected, the zero-point and tunneling corrections are different for H<sub>2</sub> and D<sub>2</sub>. At the classical saddle-point,



Table IX. Zero-point and tunneling effects on the barrier height of the  $F + H_2$  and  $F + D_2$  reactions.

$F + H_2$ surface				
	Classical Barrier		Adiabatic Barrier	
	CCI	CCI + Q	CCI	CCI + Q
$r_{HF}, a_0$	2.879	2.909	3.070	3.155
$r_{HH}, a_0$	1.447	1.445	1.425	1.421
Barrier, kcal/mole	2.888	2.143	2.639	1.860
Sym. stretch, $cm^{-1}$	3706	3768	4074	4178
Bend, $cm^{-1}$	68.5	45.9	68.5	45.9
Asym. stretch <sup>a</sup> , $cm^{-1}$	692i	605i	530i	371i
Zero-point correction <sup>b</sup> , kcal/mole	-0.602	-0.643	-0.076	-0.057
E barrier + zero point, kcal/mole	2.286	1.500	2.563	1.803
Tunneling correction, kcal/mole	-0.54	-0.47	-0.42	-0.29
Threshold, kcal/mole	1.75	1.03	2.14	1.51
$F + D_2$ surface				
	Classical Barrier		Adiabatic Barrier	
	CCI	CCI + Q	CCI	CCI + Q
$r_{HF}, a_0$	2.879	2.909	3.010	3.075
$r_{HH}, a_0$	1.447	1.445	1.430	1.427
Barrier, kcal/mole	2.888	2.143	2.761	1.997
Sym. stretch, $cm^{-1}$	2623	2667	2811	2876
Bend, $cm^{-1}$	37.7	19.1	37.7	19.1
Asym. stretch <sup>a</sup> , $cm^{-1}$	512i	448i	428i	334i
Zero-point correction <sup>b</sup> , kcal/mole	-0.488	-0.532	-0.220	-0.233
E barrier + zero point, kcal/mole	2.400	1.611	2.541	1.764
Tunneling correction, kcal/mole	-0.40	-0.35	-0.34	-0.26
Threshold, kcal/mole	2.00	1.26	2.20	1.50
<sup>a</sup> From the normal mode analysis at the classical barrier, and computed from the curvature along the Eckart potential at the adiabatic barrier.				
<sup>b</sup> For $H_2(D_2)$ we used $\omega_e=4401(3116) cm^{-1}$ , respectively, from Ref. 58.				

the barrier heights for  $H_2$  and  $D_2$  differ by 0.2 kcal/mole, whereas at the adiabatic saddle point the barriers are the same. The observation [62] of nearly identical thresholds for  $H_2$  and  $D_2$  also provides strong support for using the adiabatic barrier. In order to bring the computed threshold into agreement with experiment [62], we must lower the CCI+Q classical barrier by 0.7-0.8 kcal/mole. This produces a barrier height of 1.3-1.4 kcal/mole, or after accounting for the errors associated with these approximations, a barrier height of 1.0-1.5 kcal/mole. This is in good

agreement with the estimate made directly from the MRCI calculations, and also with that deduced in recent calculations by Truhlar and co-workers [63], although it disagrees with the value inferred by Schaefer [64] from most previous calculations.

## VII. DISCUSSION AND CONCLUSIONS

We have shown that recent developments in electronic structure calculations have given new insight into the solution of the  $n$ -particle problem and ANO basis sets have reduced the error in the one-particle basis sets. This leads to more accurate calculations than previously possible. For systems with only one heavy atom, results with an error of less than one kcal/mole are now possible. For systems with multiple bonds, the error is still a few kcal/mole.

While current calculations are capable of high accuracy, they are still computationally intensive. Therefore, it is usually not possible to fully characterize a global PES by computing a closely-spaced grid of points, and the maximum information must be extracted from the available points by a fitting procedure. At present, most dynamical methods use only a fit to the total energies; such fits to a global surface can be very difficult even when sufficient precision exists in the computed energies. One suggestion for improving the fitting procedure (without a large increase in the number of computed points) is to compute the energy derivatives, as well as the total energy, at each point on the surface. Given that analytic derivative techniques have proven far more cost-effective than the use of finite differences for locating stationary points [65], it seems likely that this could represent a major improvement in the definition of the required surfaces [66].

As illustrated by the  $F+H_2$  reaction, even the best calculations may require some scaling to reproduce experimental barrier heights, exothermicities, or reaction rates. The global surfaces obtained at a lower level of theory can also be adjusted by comparing with more accurate calibration calculations carried out at critical points on the surface. For example, the CCI+Q potential for the  $F+H_2$  reaction could be modified by comparison with more accurate MRCI calculations.

The SEC method [34] has been proposed as a way to correct for both errors in the  $n$ - and one-particle basis sets. However, its application requires a one-particle basis set with approximately the same error for the reactant and product channel. This is not easy to arrange when the basis sets are defined by a single prescription, as is the case for ANO basis sets (as seen above for  $F+H_2$ ), and is only applicable when the heats of reaction for reactants and products are known. The SEC method may be useful in estimating residual errors in less accurate calculations, especially in combination with the +Q correction so that the estimated contributions of  $n$ -particle and one-particle space incompleteness can be analyzed [67]. When ANO basis sets are used it seems preferable to use successively larger contracted sets and to obtain an estimate of the basis set limit from these results, as in the  $CH_2$  calculations described above.

The recent improvements in electronic structure calculations now make it feasible to develop of a complete PES containing one heavy atom competitive with those deduced from experimental results. Accuracies of 1 kcal/mole are often achievable for the critical points on the surface. The availability of more accurate PES should also facilitate the evaluation of dynamical methods through comparison with experiment.

## Reference

1. D. M. Cooper, R. L. Jaffe, and J. O. Arnold, *J. Spacecraft and Rockets* **22**,

- 60 (1985).
2. Pioneering the Space Frontier, The Report of the National Commission on Space, (Bantam Books 1986); also see G. Y. Anderson, AIAA Paper No. 87-2074, June 29-July 2, 1987.
3. See for example the volume of Chem. Rev. (and references there in) devoted to Chemical Dynamics; Chem. Rev. **87**, 1-288 (1987).
4. C. W. Bauschlicher, and P. R. Taylor, J. Chem. Phys. **85**, 6510 (1986).
5. C. W. Bauschlicher and S. R. Langhoff, J. Chem. Phys. **86**, 5595 (1987).
6. C. W. Bauschlicher, and P. R. Taylor, Theor. Chim. Acta **71**, 263 (1987).
7. C. W. Bauschlicher, S. R. Langhoff, H. Partridge, and P. R. Taylor, J. Chem. Phys. **85**, 3407 (1986).
8. C. W. Bauschlicher and P. R. Taylor, J. Chem. Phys. **85**, 2779 (1986).
9. C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, J. Chem. Phys. **88**, 2540 (1988).
10. "Full configuration-interaction benchmark calculations for AlH", C. W. Bauschlicher, and S. R. Langhoff, J. Chem. Phys. (in press).
11. "Full configuration-interaction study of the ionic-neutral curve crossing in LiF", C. W. Bauschlicher and S. R. Langhoff, J. Chem. Phys. (in press).
12. C. W. Bauschlicher, and S. R. Langhoff, J. Chem. Phys. **87**, 4665 (1987).
13. C. W. Bauschlicher, and P. R. Taylor, J. Chem. Phys. **86**, 858 (1987).
14. J. Almlöf and P. R. Taylor, J. Chem. Phys. **86**, 4070 (1987).
15. J. Almlöf, T. U. Helgaker and P. R. Taylor, J. Phys. Chem. **92**, 3029 (1988).
16. J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, A. J. C. Varandas in "Molecular Potential Energy Surfaces" (Wiley, New York 1984).
17. "Advances in Chemical Physics: Ab initio methods in quantum chemistry" Vol 67 and 69 (Wiley, New York, 1987)
18. S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
19. F. W. Bobrowicz and W. A. Goddard in "Methods of Electronic Structure Theory", H. F. Schaefer, ed., pp. 79, (Plenum Press, New York, 1977).
20. P. E. M. Siegbahn, A. Heiberg, B. O. Roos, B. Levy, Phys. Scr., **21**, 323 (1980); B. O. Roos, P. R. Taylor, P. E. M. Siegbahn, Chem. Phys. **48**, 157 (1980); B. O. Roos, Int. J. Quantum Chem. **S14**, 175 (1980); P. E. M. Siegbahn, J. Almlöf, A. Heiberg, B. O. Roos, J. Chem. Phys. **74**, 2384 (1981).
21. A. Bunge, J. Chem. Phys. **53**, 20 (1970); A. D. McLean and B. Liu, *ibid.* **58**, 1066 (1973); C. F. Bender and H. F. Schaefer, *ibid.* **55**, 7498 (1971).
22. H-J. Werner, E-A. Reinsch, J. Chem. Phys. **76**, 3144 (1982).
23. H-J. Werner and P. J. Knowles, J. Chem. Phys. (submitted).
24. P. E. M. Siegbahn, Int. J. Quantum Chem. **23**, 1869 (1983).
25. W. J. Hehre, L. Radom, P. von R. Schleyer and J. A. Pople "Ab initio molecular orbital theory", (Wiley, New York 1986).
26. See for example H. B. Schlegel and C. Sosa, Chem. Phys. Lett. **145**, 329 (1988).
27. S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).
28. R. Ahlrichs, P. Scharf and K. Jankowski, Chem. Phys. **98**, 381 (1985).
29. D. P. Chong and S. R. Langhoff, J. Chem. Phys. **84**, 5606 (1986).
30. R. J. Bartlett, C. E. Dykstra and J. Paldus, in "Advanced Theories and Computational Approaches to the Electronic Structure of Molecules", C. E. Dykstra, ed. p. 127 (D. Reidel, Dordrecht 1984).
31. M. R. A. Blomberg and P. E. M. Siegbahn, J. Chem. Phys. **78**, 5682 (1983).

32. J. A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
33. R. J. Gdantiz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988).
34. F. B. Brown and D. G. Truhlar, *Chem. Phys. Lett.* **117**, 307 (1985).
35. See for example R. J. Bartlett, I. Shavitt and G. D. Purvis, *J. Chem. Phys.* **71**, 281 (1979), where the addition of the +Q correction was shown to significantly increase the standard deviation for the fitted potential.
36. R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33 (1974).
37. P. Saxe, H. F. Schaefer, and N. C. Handy, *Chem. Phys. Lett.*, **79**, 202 (1981); R. J. Harrison and N. C. Handy, *ibid.* **96**, 386 (1983).
38. R. J. Bartlett, H. Sekino, and G. D. Purvis, *Chem. Phys. Lett.*, **98**, 66 (1983); W. D. Laidig and R. J. Bartlett, *ibid.* **104**, 424 (1984).
39. F. B. Brown, I. Shavitt, and R. Shepard, *Chem. Phys. Lett.*, **105**, 363 (1984).
40. P. E. M. Siegbahn, *Chem. Phys. Lett.*, **109**, 417 (1984).
41. P. J. Knowles and N. C. Handy, *Chem. Phys. Lett.*, **111**, 315 (1984).
42. W. Müller, J. Flesch and W. Meyer, *J. Chem. Phys.* **80**, 3297 (1984).
43. M. Desouter-Lecomte, J. C. Leclerc, and J. C. Lorquet, *J. Chem. Phys.* **66**, 4006 (1977); C. Galloy and J. C. Lorquet, *ibid.* 4672 (1977); B. C. Garrett, M. J. Redmon, D. G. Truhlar, and C. F. Melius, *ibid.* **74**, 412 (1981).
44. R. Grice and D. R. Herschbach, *Mol. Phys.* **27**, 159 (1974); L. R. Kahn, P. J. Hay, and I. Shavitt, *J. Chem. Phys.* **61**, 3530 (1974).
45. B. H. Lengsfeld, P. Saxe, and D. R. Yarkony, *J. Chem. Phys.* **81**, 4549 (1984); P. Saxe, B. H. Lengsfeld, and D. R. Yarkony, *Chem. Phys. Lett.* **113**, 159 (1985).
46. K. Jankowski, R. Becherer, P. Scharf, H. Schiffer and R. Ahlrichs *J. Chem. Phys.* **82** 1413 (1985).
47. R. C. Raffanetti, *J. Chem. Phys.* **58**, 4452 (1973).
48. I. Shavitt, B. J. Rosenberg, and S. Palalikit, *Int. J. Quantum Chem.* **S10**, 33 (1976).
49. S. R. Langhoff, C. W. Bauschlicher, and P. R. Taylor, *J. Chem. Phys.* **88**, 5715 (1988).
50. S. R. Langhoff and C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **86**, 6992 (1987).
51. C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, *J. Chem. Phys.* **87**, 387 (1987).
52. H.-J. Werner and E.-A. Reinsch, in "Proceedings of the 5th European Seminar on computational methods in quantum chemistry", eds P. Th. van Duijnen and W. C. Nieuwpoort (Max-Planck-Institut für Astrophysik, Munich 1981).
53. A. D. McLean, P. R. Bunker, R. M. Escibano, and P. Jensen, *J. Chem. Phys.* **87**, 2166 (1987).
54. R. D. Cowan, and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).
55. R. L. Martin, *J. Phys. Chem.* **87**, 750 (1983).
56. J. Berkowitz, J. P. Greene, H. Cho and B. Ruscic, *J. Chem. Phys.* **86**, 1235 (1987); also see K. Balasubramanian and A. D. McLean, *ibid.* **85**, 5117 (1986).
57. S. R. Langhoff, C. W. Bauschlicher, and P. R. Taylor, *Chem. Phys. Lett.* **135**, 543 (1987).
58. K. P. Huber and G. Herzberg, in "Constants of Diatomic Molecules" (Van Nostrand Reinhold, New York, 1979).

59. C. W. Bauschlicher, S. P. Walch, S. R. Langhoff, P. R. Taylor, and R. L. Jaffe, J. Chem. Phys. **88**, 1743 (1988).
60. M. J. Frisch, B. Liu, J. S. Binkley, H. F. Schaefer and W. H. Miller, Chem. Phys. Letters **114**, 1 (1985).
61. B. C. Garrett, D. G. Truhlar, R. S. Grev and A. W. Magnuson, J. Phys. Chem. **84**, 1730 (1980).
62. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden and Y. T. Lee, J. Chem. Phys. **82**, 3045 (1985) and D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer and Y. T. Lee, *ibid.* **82**, 3067 (1985).
63. D. W. Schwenke, R. Steckler, F. B. Brown and D. G. Truhlar, J. Chem. Phys. **84**, 5706 (1986) and references therein.
64. H. F. Schaefer, J. Phys. Chem. **89**, 5336 (1985).
65. P. Pulay in "Applications of Electronic Structure Theory" H. F. Schaefer, ed., pp. 153 (Plenum Press, New York, 1977).
66. B. C. Garrett, M. J. Redmon, R. Steckler, D. G. Truhlar K. K. Baldrige, D. Bartol, M. W. Schmidt, and M. S. Gordon, J. Phys. Chem. **92**, 1476 (1988).
67. D. W. Schwenke, R. Steckler, F. B. Brown and D. G. Truhlar, J. Chem. Phys. **86**, 2443 (1987).